Research and Development Laboratories of the Portland Cement Association

RESEARCH DEPARTMENT

BULLETIN 66

Effect of Aggregate on Shrinkage of Concrete and Hypothesis Concerning Shrinkage

BY
GERALD PICKETT

FEBRUARY, 1956
CHICAGO

Authorized Reprint of a Copyrighted

Journal of the American Concrete Institute
18263 W. McNichols Rd., Detroit 19, Michigan
January 1956; Proceedings Vol. 52, p. 581



Effect of Aggregate on Shrinkage of Concrete and a Hypothesis Concerning Shrinkage*

By GERALD PICKETTT

SYNOPSIS

A theoretical formula is derived for effect of aggregate on shrinkage of concrete during drying. Experiments designed to test the validity of the formula are reported.

In addition to indicating the validity of the formula, the data give the following indications: (1) First shrinkage is greater than any subsequent expansion or shrinkage resulting from moisture change. (2) At a given aggregate content the shrinkage is approximately proportional to water-cement ratio. (3) After first shrinkage, subsequent volume changes are approximately independent of water-cement ratio. (4) When shrinkages of specimens of the higher water-cement ratio are plotted against the square root of period of drying, the shapes of the curves for second shrinkage are appreciably different from those for first shrinkage in that they have considerable curvature near the origin. An explanation of these effects is given.

INTRODUCTION

A number of years ago, while at the Portland Cement Assn., the author arrived at a theoretical formula for effect of aggregate on shrinkage of concrete or mortar during drying. Experiments designed to test the validity of the formula gave results that were in fair agreement with the formula. However, certain factors in the formula which should depend on properties of the paste varied with conditions of drying and therefore led to the conclusion that the hydrated paste did not always have the same properties. The purpose of this paper is to present the theoretical formula, experimental results that were obtained, and speculations in regard to the paste that resulted from a study of the data.

DERIVATION OF FORMULA

In deriving the formula, consideration is first given to effect on shrinkage of one small, spherical particle of aggregate in a large body of concrete, the surrounding concrete considered to be a homogeneous material. This approach is similar to that of Guth¹ and Dewey,² who were concerned with the effect of fillers on elastic properties. The restraining effect of aggregate

Rd., Detroit 19, Mich.
†Member American Concrete Institute, Guest Professor of Civil Engineering, Bengal Engineering College,
West Bengal, India.

^{*}Received by the Institute Mar. 17, 1954. Title No. 52-36 is a part of copyrighted Journal of the American Concrete Institute, V. 27, No. 5, Jan. 1956, Proceedings V. 52. Separate prints are available at 50 cents each. Discussion (copies in triplicate) should reach the Institute not later than May 1, 1956. Address 18263 W. McNichols

on shrinkage of concrete was pointed out by Carlson.³ On the assumption that both the particle and the rest of the body are elastic, an expression is derived for reduction in over-all shrinkage of the body due to the one small, nonshrinking particle. This provides a formula for the effect of adding each subsequent particle if the body including all particles added previously is assumed to be homogeneous. This formula is then expressed in differential equation form and an integration made to obtain the final formula.

It will be expedient to consider that the small, spherical particle is at the center of the body of concrete which is also a sphere. If the particle is small compared to the shortest distance from it to the concrete surface, no great error will be introduced by treating the concrete as spherical with a radius equal to that distance. The restraint of the small sphere as the large sphere tends to shrink will cause the following stresses in the large sphere.⁴

$$\sigma_r = -\frac{pa^3}{r^3} \frac{b^3 - r^3}{b^3 - a^3} \dots (1)$$

$$\sigma_t = \frac{pa^3}{2r^3} \frac{b^3 + 2r^3}{b^3 - a^3} \dots \dots \dots (2)$$

where σ_r = normal stress in the radial direction

 σ_t = either of two normal stresses perpendicular to the radius

r = radial coordinate

a = radius of inner sphere

b = radius of outer sphere

p = unit pressure between inner and outer spheres

Under these conditions of spherical symmetry, radial displacement δ of any point in the outer sphere caused by the restraint of the inner sphere, and referred to the unrestrained position, is

where E and μ are Young's modulus and Poisson's ratio, respectively, for the outer sphere.

From Eq. (1), (2), and (3)

$$\delta = \frac{pa^3}{Er^2} \left[\frac{1-\mu}{2} \frac{b^3+2r^3}{b^3-a^3} + \mu \frac{b^3-r^3}{b^3-a^3} \right] \dots (4)$$

The restraint of the inner sphere has reduced the volume shrinkage of the total body by the amount

$$4\pi b^{2}\delta \bigg|_{r=b} = \frac{3p\Delta V}{E} \left(\frac{1-\mu}{2}\right) \frac{3b^{3}}{b^{3}-a^{3}} \dots (5)$$

where $\Delta V = 4/3 \pi a^3$ is the volume of the small sphere.

If the restraint had not been present, the body would have reduced in volume by 3SV, where V is its total volume and S is the unit linear shrinkage. The reduction in volume shrinkage will therefore be designated as $-3\Delta SV$, or

$$-3 \Delta SV = \frac{3p \Delta V}{E} \left(\frac{1-\mu}{2}\right) \frac{3b^3}{b^3 - a^3} \dots (6)$$

Another expression containing the pressure p will be found by considering the compressibility of the restraining particle. Reduction in volume of the

particle caused by pressure p on it will be equal to the reduced space available to it within the larger body, or

$$\frac{3(1 - 2\mu_g)p \Delta V}{E_g} = 3S \Delta V - 4\pi a^2 \delta \bigg|_{r = a} \dots (7)$$

where E_g and μ_g are the elastic constants of the particle and δ is given by Eq. (4).

Eliminating
$$p$$
 between Eq. (6) and (7) and setting $b/a = \infty$ gives $-\Delta SV = \alpha S \Delta V \dots (8)$

where

$$\alpha = \frac{3(1-\mu)}{1+\mu+2(1-2\mu_g)E/E_g} \dots (9)$$

Setting $b/a = \infty$ will introduce an error especially for particles close to the surface. However, it is believed that this error is not relatively as important as others entering this derivation.

Let volume of aggregate per unit volume of mix be g; then the increase in g due to the addition of one particle of volume ΔV to the mixture will be

$$\Delta g = \frac{gV + \Delta V}{V + \Delta V} - g = (1 - g) \frac{\Delta V}{V + \Delta V} \dots (10)$$

From Eq. (8) and (10)

$$\frac{\Delta S}{S} = -\frac{\alpha \Delta g}{1 - g} \frac{V + \Delta V}{V} \dots (11)$$

or, in differential form,

The factor α is probably a function of g since the elastic constants of the mixture, E and μ , may depend on g. But if α may be considered to be independent of g, then Eq. (12) integrates to

where S_0 is the shrinkage that would occur if no aggregate were present. For later use this equation may be written in the form

TESTS

To test the validity of the formula, $1 \times \frac{7}{8} \times 11\frac{1}{4}$ -in. prisms were prepared with various percentages of aggregate ranging from 0 percent to about 70 percent by volume. Three different types of aggregate (pulverized silica, standard Ottawa sand, and graded Elgin sand) were used to determine whether size and gradation of aggregates would also be an appreciable factor. Two cements, a high-early-strength and a normal, and two water-cement ratios were used to determine in what way the effect of aggregate might be influenced by type of cement and water-cement ratio.

TABLE 1—GENERAL OUTLINE OF CONDITIONS IN STUDY*

Cements used	Aggregates used	Percent aggregate by absolute volume† 0 5 15 30 50 65	W/C by weight
High-early- strength Laboratory mix of four brands of Type I	Silica flour Standard Ottawa sand Graded Elgin sand		0.5

*Specimens were sealed in steel molds % x 1 x 11¼ in., that were stood on end for 2 hr during setting of mortar. Each mold was turned end-for-end every 5 min. Curing was for 7 days under water at 78 F. Drying was for 224 days or longer at 50 percent relative humidity, 76 F and the wetting period was 84 days under water at 74 F. Two specimens were made of each combination, a total of 72.

†As will be noted later, there were slight deviations

from these values.

Later it was decided to investigate reversibility of volume changes of these specimens. For this purpose specimens were alternately submerged in water and dried in air. Each drying was at 50 percent relative humidity for at least 224 days and each period of wetting was 84 days. This work was begun in January, 1942, and continued for about 2 years.

Table 1 gives the general outline of conditions covered in the study.

Mixes containing up to 5 percent aggregate were too wet and those with

50 percent or more were too dry for preparation of reasonably homogeneous specimens. Repeated reversal of the position of the molds during setting tended to offset some effects of bleeding, but many of the wet mixes were blemished because of the combined effects of bleeding, shrinkage in absolute volume, and periodic turning of the molds. Some dry mixes had a high percentage of air voids though in most cases percentage of air was kept low by vigorous tamping. The wide range in plastic properties of the mixes may account for some of the nonuniformities in results.

Shrinkage during drying and expansion during wetting for the specimens made with high-early-strength cement are shown graphically in Fig. 1 and 2. Similar results were obtained with normal cement but are not shown.

Final shrinkage indicated by each curve was estimated. These results are given in Table 2.

The quantities $\log S_0/S$ and $\log 1/(1-g)$ were computed from Table 2 and plotted in Fig. 3. According to Eq. (14) the data should be represented by a straight line passing through the origin. The data for W/C=0.35 are represented fairly well by such a straight line with a slope α equal to 1.7. Various combinations of the elastic constants in Eq. (9) would make $\alpha=1.7$. A reasonable assumption that would give this value is: $\mu=0.2$, $\mu_g=0.25$, $E/E_g=0.21$.

Data for W/C = 0.50 are not represented as well by a straight line. The line shown has a slope of 1.7. Points which lie farthest from the line are for mixes that were stiff and when cast contained a considerable percentage of air voids. If these points are neglected, the agreement is excellent.

On the basis of data obtained it is concluded that the derived formula gives a good representation of the effect of aggregate on ultimate shrinkage due to change in moisture.

Other ideas suggested by the data

In addition to indicating the validity of the formula for the effect of aggregate on shrinkage, the data give the following indications: First shrinkage is greater than any subsequent expansion or shrinkage. (2) At a given aggregate content first shrinkage is approximately proportional to water-cement (3) After first ratio. shrinkage, subsequent volume changes are approximately independent water-cement ratio. When shrinkage of specimens of the higher watercement ratio is plotted against the square root of period of drying, the shapes of the curves for second shrinkage are appreciably different from those for first shrinkage in that they have considerable curvature near the origin.

In general these four indications were either not expected or not expected to the degree indicated by Fig. 1 and 2. Some of the change in behavior might have been due to carbonation during the first drying period, but the major change is believed due to other causes, as will be discussed below.

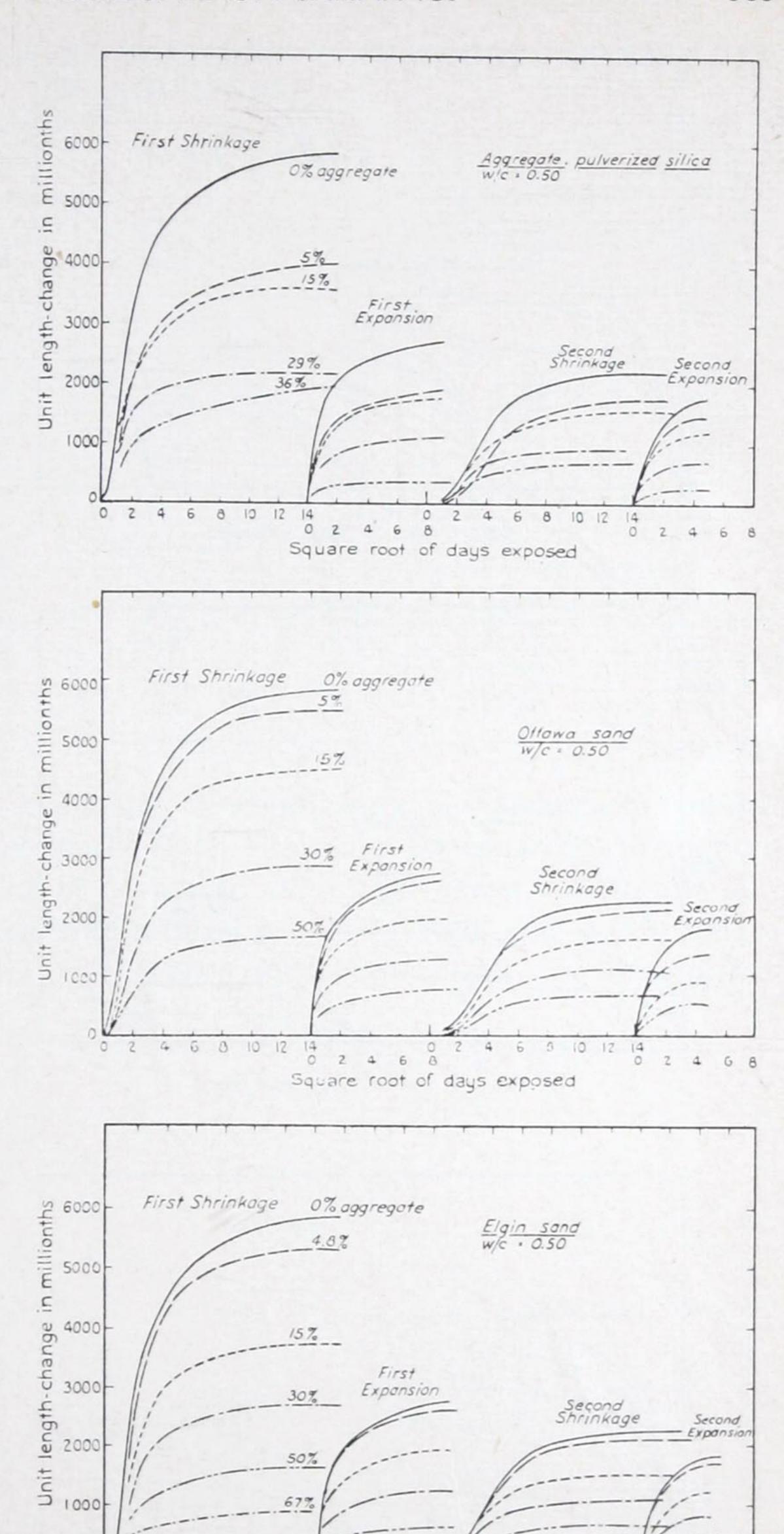
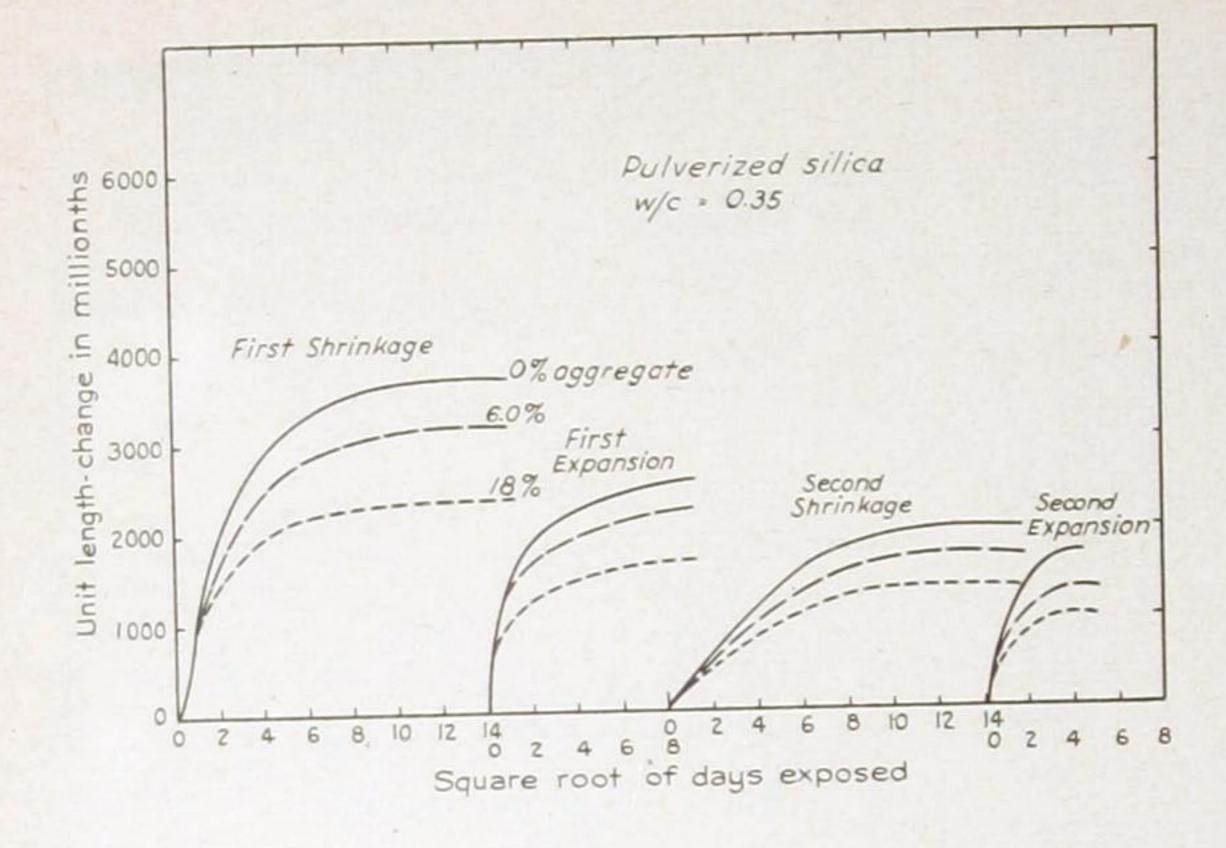
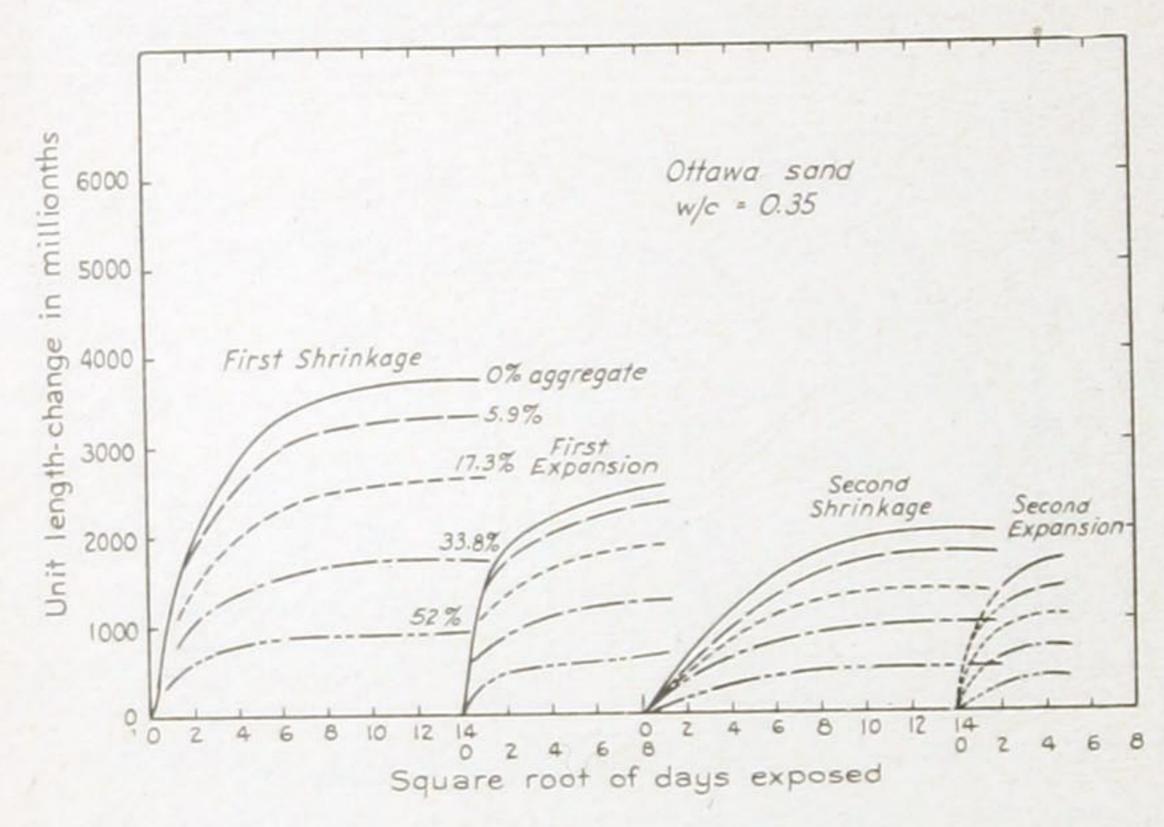


Fig. 1—Shrinkage during drying and expansion during wetting for pulverized silica, Ottawa sand, and Elgin sand using high-early-strength cement and W/C = 0.50

Square root of days exposed





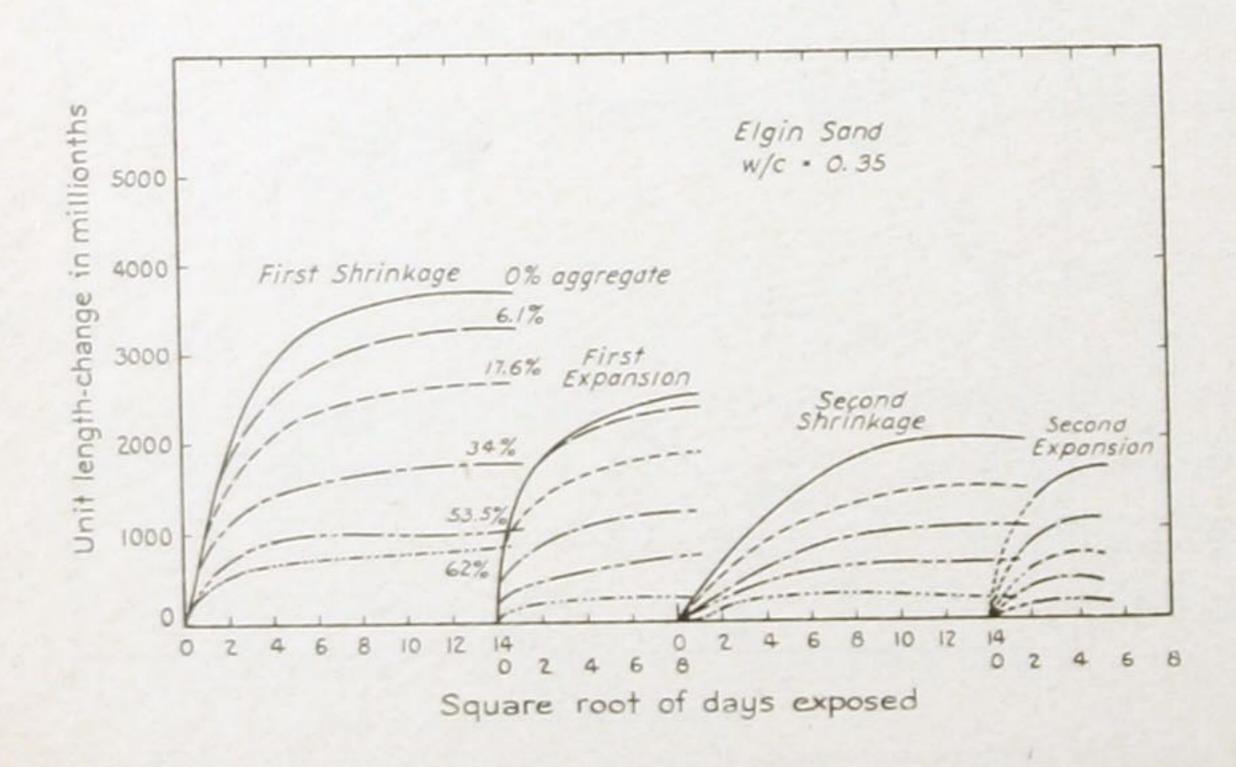


Fig. 2—Shrinkage during drying and expansion during wetting for pulverized silica, Ottawa sand, and Elgin sand using high-early-strength cement and W/C = 0.35

HYPOTHESIS ON GEL STRUCTURE

As a basis for an explanation it is proposed (1) that during first shrinkage some adjacent particles of the cement gel move closer together, whereas others move farther apart, and (2) that, in general, particles that have once made close contact will not return to their original relative positions with subsequent wetting.

No definite picture of gel structure before first shrinkage is required for this analysis except that the gel be slightly altered by the first shrinkage. As water is removed, interparticle forces will change, necessitating relative movements between particles for equilibrium of individual particles. If these relative movements for each pair of particles are not in proportion to the original distances between their centers, the arrangement will be considered to have changed.

If only discrete colloidal particles were present, shrinkage of hydrated cement might be more nearly like that of soils and show a shrinkage limit,

TABLE 2—FREE SHRINKAGE OF SPECIMENS OF VARIOUS PERCENTAGES
OF AGGREGATE

Absolute volume of aggregate per mix volume	Shrinkage in millionths						
	First shrinkage			Second shrinkage			
	Silica	Ottawa	Elgin	Silica	Ottawa	Elgin	
			W/C = 0.50				
0 0.05 0.15 0.30 0.50 0.67	5870 4000 3600 2200 2000	5870 5450 4500 2850 1700	5870 5350 3720 2700 1650 890	2180 1720 1530 950 740	2180 2100 1600 1100 670	2180 2100 1500 1100 640 410	
			W/C = 0.35				
0 0.06 0.18 0.34 0.53 0.62	3700 3230 2410 —	3700 3450 2720 1800 940	3700 3380 2690 1810 1080 900	2050 1700 1300 —	2050 1750 1380 1000 540	2050 	

i.e., down to some limiting shrinkage, it would show a shrinkage in volume comparable to the volume of water lost. However, in concrete, restraining bodies act from the beginning of drying to reduce shrinkage.³ The restraining bodies are the aggregates, unhydrated cement grains, and stable microcrystalline products of hydration. There would, of course, be some differ-

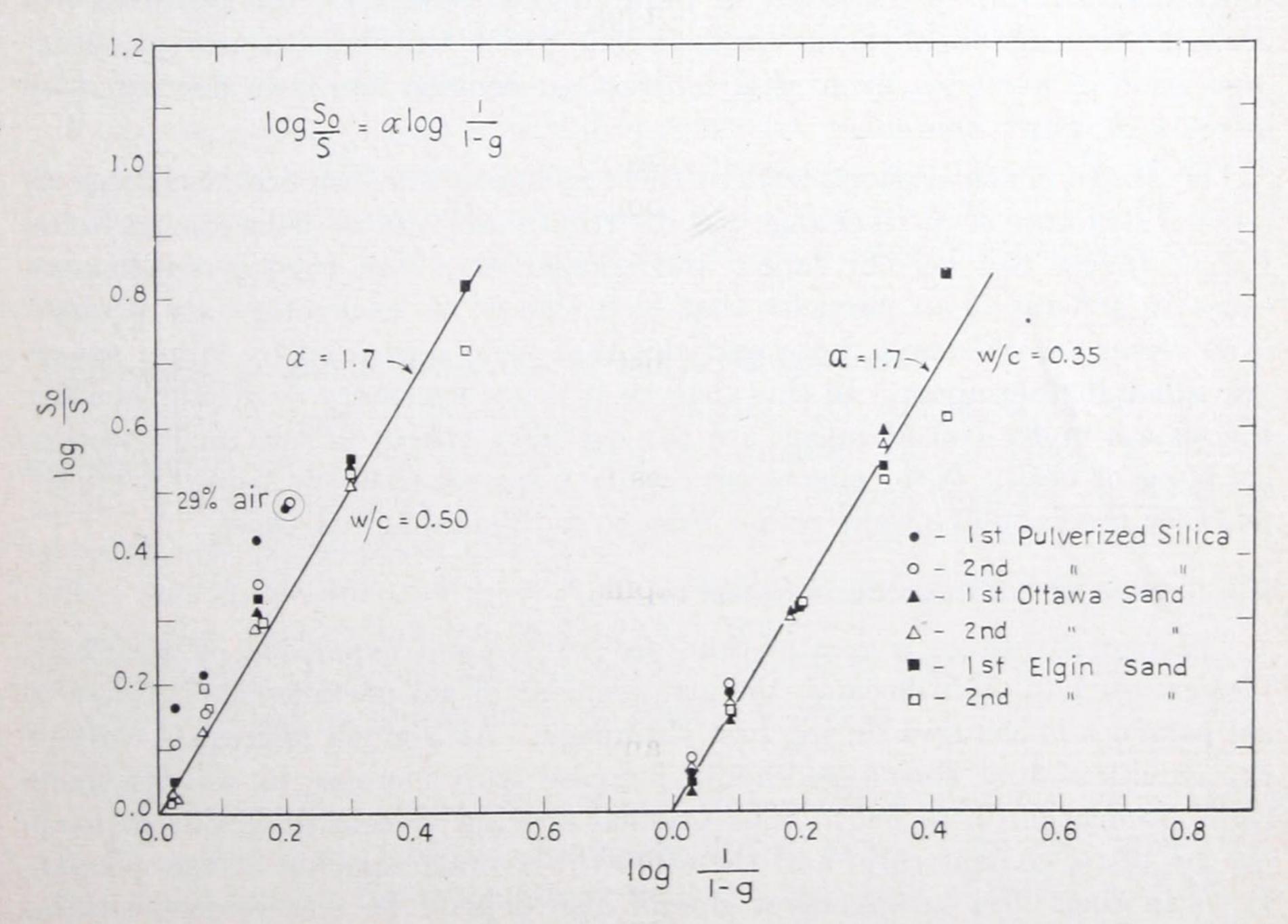


Fig. 3—Effect of aggregate on shrinkage

ence in the intrinsic shrinkage of cement gel and soil because of the bonds between gel particles. Experiments show that concrete shrinkage instead of being about equal to volume of water lost is ordinarily only about 2 to 7 percent as much. When shrinkage is not equal to loss of water, spaces will form and hydrostatic tension must result. A given gel particle will be under tensile forces tending to pull it toward adjacent particles. These forces may be intense, as is shown below by the relation between hydrostatic tension and relative humidity. Under the conditions for which Kelvin's equation for the curvature of a meniscus in equilibrium with its vapor applies, the intensity of hydrostatic tension of water at room temperature is given by

 $T = -19,600 \log_e h$

where T = hydrostatic tension in psi

h = relative humidity

For example, if h = 0.98, T = 392 psi and if h = 0.50, T = 13,600 psi. Kelvin's equation probably is not applicable when radius of curvature is only a few molecular diameters.

Under the action of forces of hydrostatic origin some adjacent particles will be pulled or pushed closer together while other adjacent particles will be pulled farther apart. As two adjacent particles are brought closer together, large compressive forces at the points of closest approach will naturally arise from intermolecular repulsion. These compressive forces should increase with increase in nearby tensile forces so that the particles remain in static equilibrium. As a result of high contact pressures, the particles will probably develop chemical or surface bonds which will tend to prevent future separation of particles, even after hydrostatic tension has been decreased by increase in water content.

The above considerations lead to the conclusion that the first shrinkage alters gel structure so as to change size distribution of spaces between particles. Larger spaces will become larger and smaller ones will become smaller because in general those particles that were closest to each other are brought even closer together and those particles that were separated by larger spaces are pulled farther apart. In this analysis it is not necessary to decide whether the spaces under consideration are the capillary spaces or the much smaller gel pores or both. If the spaces are capillary spaces, then the word "particle" refers to the capillary walls rather than to individual gel particles.

Application of the hypothesis to test results

The first shrinkage is greater than any subsequent expansion or shrinkage (indication 1, p. 585) because the arrangement of gel particles and groups of gel particles is changed during first shrinkage. At a given aggregate content the extent of first shrinkage should increase with increase in water-cement ratio (indication 2, p. 585). The original spacing of cement grains depends on the water-cement ratio and therefore the average spacing of the gel particles in their first arrangement should also depend on water-cement ratio. More motion during first shrinkage is possible with greater spacing.

After the first shrinkage subsequent volume changes are approximately independent of water-cement ratio (indication 3, p. 585) because after once having been dried the spacing between adjacent gel particles should be more a function of humidity and of the corresponding degree of drying than of original spacing. The gels from mixes of higher water-cement ratio will have a more open structure between agglomerations of particles but not necessarily any greater capacity for changes in volume. This last statement is in accord with the conception of gel structure given by Powers. On the basis of various experiments he concludes that the gel substance has a characteristic spacing of the gel particles.^{5,6,7}

The difference in shape of the curves for first and subsequent shrinkages (indication 4, p. 585) is attributed to both the change in distribution of capillary sizes and to the fact that stabilization takes place during first shrinkage but does not occur appreciably during subsequent shrinkages. In any given region in the specimen most of the water in the larger capillaries must be lost before appreciable hydrostatic tension can be developed. During the first shrinkage, before gel structure has become stabilized, appreciable shrinkage can take place with little hydrostatic tension. But after the gel has become stabilized, larger interparticle forces are required to produce comparable shrinkages. The pastes of lower water-cement ratio do not have many large capillaries and therefore, in drying, soon reach the linear portion of the shrinkage versus square-root-of-time relation even though the gel has been stabilized. Moreover, the gels in pastes of low water-cement ratio undergo relatively little structural change during first shrinkage because of the original close particle spacing.

From the above picture it would appear that all volume changes after the first shrinkage should be fairly reversible; however, shrinkage stresses resulting from nonuniform drying or wetting and chemical changes will no doubt cause some change in the structure and therefore prevent complete reversibility.

Explanation of plastic properties of hardened concrete

As noted by many investigators, concrete has the capacity for a comparatively large amount of creep and the apparent rate of creep for a given stress is relatively large if loads are applied during drying. Although an attempt was made in an earlier paper⁸ to show that at least a part of this effect was a natural consequence of nonuniform shrinkage and a nonlinear stress-creep relationship, no satisfactory explanation has been given for the large capacity for creep without failure in tension (cracking) that concrete has while drying as compared to its smaller capacity for creep before or after drying.

By assuming that gel particles change their relative positions, some making closer contacts and others separating during drying, we can understand the large capacity for creep which concrete has while drying. The picture is that each small community of particles will undergo considerable distor-

tional deformation. However, because these deformations are miscellaneously orientated, a region consisting of many such small communities will apparently have no distortion. But if a small stress in a given direction is added, the region will have a resultant distortion which could be of considerable magnitude if high interparticle stresses are also present. After the gel particles have acquired stable positions, the rate of creep will be much less for a given stress and the capacity for creep will be materially reduced, for the action just described cannot take place.

ACKNOWLEDGMENTS

Except for minor revisions, this paper was written in 1944 while the author was at the Portland Cement Assn. working under the direct supervision of T. C. Powers. Credit is due Mr. Powers and the Portland Cement Assn. not only for the work here reported but for urging that the paper be submitted for publication.

REFERENCES

1. Guth, E., "Theory of Filler Reinforcement," Journal of Applied Physics, V. 16, Jan. 1945, p. 20.

2. Dewey, J. M., "Elastic Constants of Materials Loaded with Non-Rigid Fillers," Journal

of Applied Physics, V. 18, June 1947, pp. 578-581.

3. Carlson, R. W., "Drying Shrinkage of Large Concrete Members," ACI Journal, Jan.-Feb. 1937, Proc. V. 33, p. 332.

4. Timoshenko, S., and Goodier, J. N., Theory of Elasticity, 2nd Edition, McGraw-Hill

Book Co., Inc., New York, 1951, p. 359.

5. Powers, T. C., and Brownyard, T. L., "Physical Properties of Hardened Portland Cement Paste," ACI Journal, Feb. 1947, Proc. V. 43, pp. 495 and 704-706.

6. Powers, T. C., "A Working Hypothesis for Further Studies of Frost Resistance of Concrete," ACI Journal, Feb. 1945, Proc. V. 41, p. 246.

- 7. Powers, T. C., and Helmuth, R. A., "Theory of Volume Changes in Hardened Portland Cement Paste During Freezing," *Proceedings*, Highway Research Board, V. 32, 1953, p. 285.
- 8. Pickett, G., "The Effect of Moisture Content on the Creep of Concrete under a Sustained Load," ACI Journal, Feb. 1942, Proc. V. 38, p. 333.

For such discussion of this paper as may develop please see Part 2, December 1956 JOURNAL. In Proceedings V. 52 discussion immediately follows the June 1956 JOURNAL pages.

Bulletins Published by the Research Department Research and Development Division of the

Portland Cement Association

Bulletin 1-"Estimation of Phase Composition of Clinker in the System 3CaO. SiO₂-2CaO·SiO₂-3CaO·Al₂O₃-4CaO·Al₂O₃·Fe₂O₃ at Clinkering Temperatures," by L. A. Dahl, May, 1939.

Reprinted from Rock Products, 41, No. 9, 48; No. 10, 46; No. 11, 42; No. 12, 44 (1938); 42, No. 1, 68; No. 2, 46; No. 4, 50 (1939).

- Bulletin 2—"The Bleeding of Portland Cement Paste, Mortar and Concrete Treated as a Special Case of Sedimentation," by T. C. Powers; with an appendix by L. A. Dahl; July, 1939.
- Bulletin 3-"Rate of Sedimentation: I. Nonflocculated Suspensions of Uniform Spheres; II. Suspensions of Uniform-Size Angular Particles; III. Concentrated Flocculated Suspensions of Powders"; by HAROLD H STEINOUR, October, 1944.

Reprinted from Industrial and Engineering Chemistry, 36, 618, 840, 901 (1944).

- Bulletin 4—"Further Studies of the Bleeding of Portland Cement Paste," by HAROLD H. Steinour, December, 1945.
- Bulletin 5-"A Working Hypothesis for Further Studies of Frost Resistance of Concrete," by T. C. Powers, February, 1945.

Reprinted from Journal of the American Concrete Institute (February, 1945); Proceedings, 41, 245 (1945).

- Bulletin 5A-Supplement to Bulletin 5; Discussion of the paper "A Working Hypothesis for Further Studies of Frost Resistance of Concrete," by T. C. Powers; discussion by: Ruth D. Terzaghi, Douglas McHenry, H. W. Brewer, A. R. Collins, and Author; March, 1946. Reprinted from Journal of the American Concrete Institute Supplement (November 1945); Proceedings, 41, 272-1 (1945).
- Bulletin 6—"Dynamic Testing of Pavements," by GERALD PICKETT, April, 1945. Reprinted from Journal of the American Concrete Institute (April, 1945); Proceedings, 41, 473 (1945).
- Bulletin 7—"Equations for Computing Elastic Constants from Flexural and Torsional Resonant Frequencies of Vibration of Prisms and Cylinders," by Gerald Pickett, September, 1945.

Reprinted from Proceedings, American Society for Testing Materials, 45, 846 (1945); discussion, 864.

- Bulletin 8—"Flexural Vibration of Unrestrained Cylinders and Disks," by GERALD Pickett, December, 1945. Reprinted from Journal of Applied Physics, 16, 820 (1945).
- Bulletin 9-"Should Portland Cement Be Dispersed?" by T. C. Powers, February, 1946. Reprinted from Journal of the American Concrete Institute (November, 1945); Proceedings, 42, 117 (1946).
- Bulletin 10—"Interpretation of Phase Diagrams of Ternary Systems," by L. A. Dahl, March, 1946. Reprinted from The Journal of Physical Chemistry, 50, 96 (1946).
- Bulletin 11-"Shrinkage Stresses in Concrete: Part 1-Shrinkage (or Swelling), Its Effect upon Displacements and Stresses in Slabs and Beams of Homogeneous, Isotropic, Elastic Material; Part 2-Application of the Theory Presented in Part 1 to Experimental Results"; by GERALD PICKETT, March, 1946.

Reprinted from Journal of the American Concrete Institute (January and February,

1946); Proceedings, 42, 165, 361 (1946).

Bulletin 12—"The Influence of Gypsum on the Hydration and Properties of Portland Cement Pastes," by William Lerch, March, 1946.

Reprinted from Proceedings, American Society for Testing Materials, 46, 1251 (1946).

Bulletin 13—"Tests of Concretes Containing Air-Entraining Portland Cements or Air-Entraining Materials Added to Batch at Mixer," by H. F. Gonner-Man, April, 1947.

Reprinted from Journal of the American Concrete Institute (June, 1944); Proceedings, 40, 477 (1944); also supplementary data and analysis, reprinted from Supplement (November, 1944); Proceedings, 40, 508-1 (1944).

Bulletin 14—"An Explanation of the Titration Values Obtained in the Merriman Sugar-Solubility Test for Portland Cement," by WILLIAM LERCH, March, 1947.

Reprinted from ASTM Bulletin, No. 145, 62 (March, 1947).

Bulletin 15—"The Camera Lucida Method for Measuring Air Voids in Hardened Concrete," by George J. Verbeck, May, 1947.

Reprinted from Journal of the American Concrete Institute (May, 1947); Proceedings, 43, 1025 (1947).

Bulletin 16—"Development and Study of Apparatus and Methods for the Determination of the Air Content of Fresh Concrete," by Carl A. Menzel, May, 1947.

Reprinted from Journal of the American Concrete Institute (May, 1947); Proceedings, 43, 1053 (1947).

- Bulletin 17—"The Problem of Proportioning Portland Cement Raw Mixtures:
 Part I—A General View of the Problem; Part II—Mathematical Study
 of the Problem; Part III—Application to Typical Processes; Part IV—
 Direct Control of Potential Composition"; by L. A. Dahl, June, 1947.

 Reprinted from Rock Products, 50, No. 1, 109; No. 2, 107; No. 3, 92; No. 4, 122 (1947).
- Bulletin 18—"The System CaO-SiO₂-H₂O and the Hydration of the Calcium Silicates," by Harold H. Steinour, June, 1947.

 Reprinted from Chemical Reviews, 40, 391 (1947).
- Bulletin 19—"Procedures for Determining the Air Content of Freshly-Mixed Concrete by the Rolling and Pressure Methods," by CARL A. MENZEL, June, 1947.

Reprinted from Proceedings, American Society for Testing Materials, 47, 833 (1947).

Bulletin 20—"The Effect of Change in Moisture-Content on the Creep of Concrete under a Sustained Load," by Gerald Pickett, July, 1947.

Reprinted from Journal of the American Concrete Institute (February, 1942); Proceedings, 38, 333 (1942).

Bulletin 21—"Effect of Gypsum Content and Other Factors on Shrinkage of Concrete Prisms," by Gerald Pickett, October, 1947.

Reprinted from Journal of the American Concrete Institute (October, 1947); Proceedings, 44, 149 (1948).

Bulletin 22—"Studies of the Physical Properties of Hardened Portland Cement Paste," by T. C. Powers and T. L. Brownyard, March, 1948.

Reprinted from Journal of the American Concrete Institute (October-December, 1946; January-April, 1947); Proceedings, 43, 101, 249, 469, 549, 669, 845, 933 (1947).

Bulletin 23—"Effect of Carbon Black and Black Iron Oxide on Air Content and Durability of Concrete," by Thomas G. Taylor, May, 1948.

Reprinted from Journal of the American Concrete Institute (April, 1948); Proceedings, 44, 613 (1948).

Bulletin 24—"Effect of Entrained Air on Concretes Made with So-Called 'Sand-Gravel' Aggregates," by Paul Klieger, November, 1948.

Reprinted from Journal of the American Concrete Institute (October, 1948); Proceedings, 45, 149 (1949).

Bulletin 25—"A Discussion of Cement Hydration in Relation to the Curing of Concrete," by T. C. Powers, August, 1948.

Reprinted from Proceedings of the Highway Research Board, 27, 178 (1947).

Bulletin 26—"Long-Time Study of Cement Performance in Concrete." This bulletin comprises four installments of the report of this investigation, by F. R. McMillan, I. L. Tyler, W. C. Hansen, William Lerch, C. L. Ford, and L. S. Brown, August, 1948.

Reprinted from Journal of the American Concrete Institute (February-May, 1948);

Proceedings, 44, 441, 553, 743, 877 (1948).

Bulletin 27—"Determination of the Air Content of Mortars by the Pressure Method," by Thomas G. Taylor, February, 1949.

Reprinted from ASTM Bulletin, No. 155, 44 (December, 1948).

Bulletin 28—"A Polarographic Method for the Direct Determination of Aluminum Oxide in Portland Cement," by C. L. Ford and Lorrayne Le Mar, April, 1949.

Reprinted from ASTM Bulletin, No. 157, 66 (March, 1949).

- Bulletin 29—"The Nonevaporable Water Content of Hardened Portland-Cement Paste—Its Significance for Concrete Research and Its Methods of Determination," by T. C. Powers, June, 1949.

 Reprinted from ASTM Bulletin, No. 158, 68 (May, 1949).
- Bulletin 30—"Long-Time Study of Cement Performance in Concrete—Chapter 5.

 Concrete Exposed to Sulfate Soils," by F. R. McMillan, T. E. Stanton,
 I. L. Tyler and W. C. Hansen, December, 1949.

 Reprinted from a Special Publication of the American Concrete Institute (1949).
- Bulletin 31—"Studies of Some Methods of Avoiding the Expansion and Pattern Cracking Associated with the Alkali-Aggregate Reaction," by WILLIAM LERCH, February, 1950.

Reprinted from Special Technical Publication No. 99, published by American Society for Testing Materials (1950).

- Bulletin 32—"Long-Time Study of Cement Performance in Concrete—Chapter 6.

 The Heats of Hydration of the Cements," by George J. Verbeck and Cecil W. Foster, October, 1949.

 Reprinted from Proceedings, American Society for Testing Materials, 50, 1235 (1950).
- Bulletin 33—"The Air Requirement of Frost-Resistant Concrete," by T. C. Powers; discussion by T. F. Willis.

 Reprinted from Proceedings of the Highway Research Board, 29, 184 (1949).
- Bulletin 34—"Aqueous Cementitious Systems Containing Lime and Alumina," by Harold H. Steinour, February, 1951.
- Bulletin 35—"Linear Traverse Technique for Measurement of Air in Hardened Concrete," by L. S. Brown and C. U. Pierson, February, 1951.

 Reprinted from Journal of the American Concrete Institute (October, 1950); Proceedings, 47, 117 (1951).
- Bulletin 36—"Soniscope Tests Concrete Structures," by E. A. WHITEHURST, February, 1951.

 Reprinted from Journal of the American Concrete Institute (February, 1951); Proceedings 47, 433 (1951).
- Bulletin 37—"Dilatometer Method for Determination of Thermal Coefficient of Expansion of Fine and Coarse Aggregate," by George J. Verbeck and Werner E. Hass, September, 1951.

 Reprinted from Proceedings of the Highway Research Board, 30, 187 (1951).
- Bulletin 38—"Long-Time Study of Cement Performance in Concrete—Chapter 7. New York Test Road," by F. H. Jackson and I. L. Tyler, October, 1951.

 Reprinted from Journal of the American Concrete Institute (June, 1951); Proceedings 47, 773 (1951).
- Bulletin 39—"Changes in Characteristics of Portland Cement as Exhibited by Laboratory Tests Over the Period 1904 to 1950," by H. F. Gonnerman and William Lerch.

Reprinted from Special Publication No. 127 published by American Society for Testing Materials.

- Bulletin 40—"Studies of the Effect of Entrained Air on the Strength and Durability of Concretes Made with Various Maximum Sizes of Aggregate," by Paul Klieger.

 Reprinted from Proceedings of the Highway Research Board, 31, 177 (1952).
- Bulletin 41—"Effect of Settlement of Concrete on Results of Pull-Out Bond Tests," by Carl A. Menzel, November, 1952.
- Bulletin 42—"An Investigation of Bond Anchorage and Related Factors in Reinforced Concrete Beams," by CARL A. MENZEL and WILLIAM M. WOODS, November, 1952.

Bulletin 43—"Ten Year Report on the Long-Time Study of Cement Performance in Concrete," by Advisory Committee of the Long-Time Study of Cement Performance in Concrete, R. F. Blanks, Chairman.

Reprinted from Journal of the American Concrete Institute (March, 1953); Proceedings,

49, 601 (1953).

Bulletin 44—"The Reactions and Thermochemistry of Cement Hydration at Ordinary Temperature," by Harold H. Steinour.

Reprinted from Third International Symposium on the Chemistry of Cement. London. Sept. 1952.

- Bulletin 45—"Investigations of the Hydration Expansion Characteristics of Portland Cement," by H. F. Gonnerman, Wm. Lerch, and Thomas M. Whiteside, June, 1953.
- Bulletin 46—"Theory of Volume Changes in Hardened Portland Cement Paste During Freezing," by T. C. Powers and R. A. Helmuth.

 Reprinted from Proceedings of the Highway Research Board, 32, 285 (1953).
- Bulletin 47—"The Determination of Non-Evaporable Water in Hardened Portland Cement Paste," by L. E. Copeland and John C. Hayes.

 Reprinted from ASTM Bulletin No. 194, 70 (December, 1953).
- Bulletin 48—"The Heats of Hydration of Tricalcium Silicate and beta-Dicalcium Silicate," by Stephen Brunauer, J. C. Hayes and W. E. Hass.

 Reprinted from The Journal of Physical Chemistry, 58, 279 (1954).
- Bulletin 49—"Void Spacing as a Basis for Producing Air-Entrained Concrete," by T. C. Powers.

 Reprinted from Journal of the American Concrete Institute (May, 1954); Proceedings, 50, 741 (1954).
- Bulletin 49A—Discussion of the paper "Void Spacing as a Basis for Producing Air-Entrained Concrete," by J. E. Backstrom, R. W. Burrows, V. E. Wolkodoff and Author, T. C. Powers.

 Reprinted from Journal of the American Concrete Institute (Dec., Part 2, 1954); Pro-
- Bulletin 50-"The Hydrates of Magnesium Perchlorate," by L. E. Copeland and R. H. Bragg.

ceedings, 50, 760-1 (1954).

Reprinted from The Journal of Physical Chemistry, 58, 1075 (1954).

- Bulletin 51—"Determination of Sodium and Potassium Oxides in Portland Cement Raw Materials and Mixtures, and Similar Silicates by Flame Photometry," by C. L. FORD.

 Reprinted from Analytical Chemistry, 46, 1578 (1954).
- Bulletin 52—"Self Desiccation in Portland Cement Pastes," by L. E. Copeland and R. H. Bragg.

 Reprinted from ASTM Bulletin, No. 204, 34 (February, 1955).
- Bulletin 53—"Permeability of Portland Cement Pastes," by T. C. Powers, L. E. Cope-Land, J. C. Hayes and H. M. Mann.

 Reprinted from Journal of the American Concrete Institute, (November, 1954); Proceedings, 51, 285 (1955).
- Bulletin 54—"Some Observations on the Mechanics of Alkali-Aggregate Reaction," by L. S. Brown.

Reprinted from ASTM Bulletin, No. 205, 40 (April, 1955).

Bulletin 55—"An Interpretation of Published Researches on the Alkali-Aggregate Reaction: Part 1—The Chemical Reactions and Mechanism of Expansion; Part 2—A Hypothesis Concerning Safe and Unsafe Reactions with Reactive Silica in Concrete," by T. C. Powers and H. H. Steinour.

Reprinted from Journal of the American Concrete Institute (February and April, 1955); Proceedings, 51, 497, 785 (1955).

Bulletin 56—"Comparison of Results of Three Methods for Determining Young's Modulus of Elasticity of Concrete," by R. E. PHILLEO.

Reprinted from Journal of the American Concrete Institute (January, 1955); Proceedings 51, 461 (1955).

Bulletin 57-"Osmotic Studies and Hypothesis Concerning Alkali-Aggregate Reaction," by George J. Verbeck and Charles Gramlich.

Reprinted from Proceedings, American Society for Testing Materials, 55, (1955).

Bulletin 58—"Basic Considerations Pertaining to Freezing and Thawing Tests," by T. C. Powers

Reprinted from Proceedings, American Society for Testing Materials, 55, (1955).

Bulletin 59-"New Study on Reactions in Burning Cement Raw Materials," by L. A. DAHL.

Reprinted from Rock Products, 58, No. 5, 71; No. 6, 102; No. 7, 78 (1955).

- Bulletin 60-"Long-Time Study of Cement Performance in Concrete-Chapter 9. Correlation of the Results of Laboratory Tests with Field Performance Under Natural Freezing and Thawing Conditions," by F. H. JACKSON. Reprinted from Journal of the American Concrete Institute (October, 1955); Proceedings 52, 159 (1956).
- Bulletin 61-"A Method for the Determination of the Cement Content of Plastic Concrete," by W. G. HIME and R. A. WILLIS. Reprinted from ASTM Bulletin No. 209, 37 (October, 1955).
- Bulletin 62-"Investigation of the Franke Method of Determining Free Calcium Hydroxide and Free Calcium Oxide," by E. E. PRESSLER, STEPHEN BRU-NAUER and D. L. KANTRO. Reprinted from Analytical Chemistry, Vol. 00, p. 00, 1955.
- Bulletin 63-"Hydraulic Pressure in Concrete," by T. C. Powers. Reprinted from Proceedings, American Society of Civil Engineers, 81, 742 (July, 1955).
- Bulletin 64-"The Freezing and Thawing Test," by T. C. POWERS. Reprinted from ASTM Report on Significance of Tests of Concrete and Concrete Aggregates, 3rd. Edition, 1955.
- Bulletin 65-"The Stoichiometry of the Hydration of Tricalcium Silicate at Room Temperature: I-Hydration in a Ball Mill; II-Hydration in a Paste Form," by Stephen Brunauer, L. E. Copeland and R. H. Bragg. Reprinted from The Journal of Physical Chemistry, Vol. 60 p. 112 (January, 1956).
- Bulletin 66-"Effect of Aggregate on Shrinkage of Concrete and Hypothesis Concerning Shrinkage, "by GERALD PICKETT. Reprinted from Journal of the American Concrete Institute (January, 1956); Proceed-

ings, 52, p. 581 (1956).

